TECHNICAL NOTES

A COMPARISON OF THE TANNING ACTION OF DITHIORESORCINOL AND RESORCINOL

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INTRODUCTION

Resorcinol and formaldehyde have been used to produce leather by an *in situ* tannage (1). The preferred conditions are a ratio of three moles of formaldehyde to one of resorcinol at a pH of 0.5 to 1.5, although satisfactory leather can be produced by raising the pH gradually to about 8.0 (2). A Mannich reaction yielding covalent cross-links has been postulated to account for the high hydrothermal stability of the leather.

It is of some theoretical interest to compare the sulfur analogue of resorcinol, namely dithioresorcinol, with resorcinol in the same procedure.

PROCEDURE

Dithioresorcinol was prepared by the Eastman Kodak Company under contract with the Eastern Regional Research Laboratory of the U. S. Department of Agriculture. Sulfur analysis: Theory 45 percent, found 44.97 percent.

A solution was prepared consisting of 12.5 ml. of water, 12.5 ml. of ethanol, 2.5 g. of sodium chloride, 6.4 ml. (0.0452 mole) of dithioresorcinol and 11 ml. (0.1356 mole) of formaldehyde as formalin. A 50 g. piece of pickled Cabretta sheepskin was added and the container was tumbled on a revolving machine. Formaldehyde alone and resorcinol and formaldehyde were used in the same procedure as controls. The solutions were acidified gradually to a pH of 0.5 to 0.7, run continuously overnight and shrink temperatures (Ts) determined.

A similar series was run, raising the pH gradually to about 8.5.

RESULTS

After one day, the Ts of the dithioresorcinol-formaldehyde skin in acid solution was 37°C. Tanning was continued for 13 days during which the Ts rose gradually to a constant Ts of 68°C. The resorcinol-formaldehyde-tanned skin did not shrink in boiling water in five minutes after tanning overnight.

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Formaldehyde alone did not tan at this very low pH. The dithioresorcinol-formaldehyde-tanned skin was flaccid and not tanned by practical standards whereas the resorcinol-formaldehyde-tanned skin was normal leather with a pink color at a pH of 0.5 and a light tan color at a pH of 3.5.

In alkaline solution the dithioresorcinol-formaldehyde sample had a Ts of 63°C. after one day, which rose to a constant T_s of 71°C. in six days. The resorcinol-formaldehyde-tanned sample had a T_s of 100°C. in one day. The use of formaldehyde alone gave a T_s of 84°C. The dithioresorcinol-formaldehyde skin had a bluish-gray color and was flaccid like the formaldehyde-tanned skin. The resorcinol-formaldehyde-tanned skin had the typical dark brown color of this tannage on the alkaline side.

DISCUSSION

A mixture of water and ethanol was used to partially dissolve the dithioresorcinol. This did not interfere with the resorcinol-formaldehyde tannage. The initial test using water only gave entirely negative results with dithioresorcinol, due to the insolubility of mercaptans in water.

It is apparent that the tanning action of thioresorcinol with formaldehyde is not comparable to that of resorcinol and formaldehyde. The Ts did rise moderately at a pH of 0.5–0.7 over a long period of time which indicated that some reaction took place, but normal leather was not produced. On the alkaline side the Ts was, if anything, lower than that obtainable with formaldehyde alone. The thiol groups in the meta position in dithioresorcinol do not have the activating effect in the positions ortho to one group and para to the other which exists in resorcinol.

REFERENCES

1. Windus, W. *JALCA,* 47, 87 (1952).
2. van Vlimmeren, P. J. *J.S.L.T.C.,* 47, 65 (1963).